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(54) Title: A PROCESS FOR PREPARING POLYURETHANE FOAM IN THE PRESENCE OF A HYDROCARBON BLOWING AGENT

(57) Abstract

Disclosed is a process for preparing a rigid, hydrocarbon-blown, polyurethane foam by reacting a polyisocyanate with a polyurethane precursor composition comprising a polyol and a compatibilizing agent containing a compatibilizing radical of the formula: $-(C_nH_{2n+1})$ wherein n is a number greater than or equal to 5, and wherein the compatibilizing agent contains at least one active hydrogen atom, provided that there is no more than one aromatic group per molecule, and further wherein the compatibilizing agent is a fat, oil, monoglyceride, diglyceride, fatty acid, fatty alcohol, fatty amide, fatty amine, fatty acid ester, alkoxyated adduct of any of the foregoing, alkyl phenol or propoxyated adduct thereof, alkyl phenol or adduct thereof with ethylene oxide and propylene oxide, alkyl phenol or adduct thereof with less than an average of four molecules of ethylene oxide per molecule of alkyl phenol or a mixture thereof. A preferred compatibilizing agent is castor oil. The compatibilizing agent enhances the miscibility of the hydrocarbon blowing agent. Advantageously, the polyurethane precursor compositions exhibit improved storage stability.

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A PROCESS FOR PREPARING POLYURETHANE FOAM IN THE PRESENCE OF A HYDROCARBON BLOWING AGENT

This invention relates to a process for preparing a rigid, hydrocarbon blown, polyurethane foam by reacting a polyisocyanate with a polyol composition comprising a material which compatibilizes the hydrocarbon in the polyurethane formulation.

A recent trend in the manufacture of polyurethane foam, especially rigid polyurethane foam, is the use of hydrocarbon blowing agents as substitute or replacement for the traditionally employed blowing agents including trichlorofluoromethane. Such trend has been motivated by the desire to eliminate the use of certain fully halogenated alkanes in an effort to protect the environment including the ozone content of the atmosphere. The general use of hydrocarbons as a blowing agent for polyurethane foam is widely reported in the literature. For example, U.S. Patent 5,096,933 discloses the use of cyclopentane, cyclohexane or mixtures thereof. U.S. Patent 5,182,309 discloses the use of pentane. U.S. Patent 5,001,164 discloses the use of pentane in combination with trichloroethane. U.S. Patent 5,286,759 discloses combinations of hydrocarbons containing at least 4 carbon atoms with perfluoroalkanes as a blowing agent for polyurethane foam manufacture. U.S. Patent 4,263,412 discloses the preparation of polyurethane foam in the presence of butane. Of the mentioned hydrocarbons, use of cyclopentane and pentane is presently favored due to availability and general benefit to the physical properties of the foam.

However, to prepare polyurethane foam which exhibits attractive physical properties, advantageously all reactants should be readily miscible with one another and/or high efficiency mixing procedures be employed to ensure even distribution of all starting materials. In the presence of poor miscibility or poor mixing, the resulting foam may exhibit inferior, unattractive, physical properties. Hydrocarbon blowing agents, especially when used in significant amounts as might be required to produce a low density foam, are generally not noted for having attractive miscibility with the majority of polyester or polyether polyols commonly used to prepare polyurethane foam. Frequently separation results leading to poor mixing and/or poor foam quality.

In the art when problems of miscibility are encountered, using the traditional type of blowing agents, frequently they can be resolved by varying the amount of cell stabilizing agent or surfactant present in the foaming process. In many instances, the problem has been resolved by use of a surfactant in an amount of from 0.1 to 2 parts per 100 parts of polyol. Use of greater amounts of surfactants, normally a mineral oil of the polysiloxane type, can lead to a significant decline in the physical properties of the resulting foam. For closed-cell rigid polyurethane foam, this can be a reduction of compressive strength, a loss of thermal insulation potential as a consequence of an acquired open-cell content, or poor mold filling (flow) characteristics. When preparing low density polyurethane foam in the presence of a

hydrocarbon blowing agent with elevated loadings of the conventional surfactants, the poor miscibility problem is not satisfactorily resolved. Accordingly it would be desirable to provide for an alternative foaming process permitting the manufacture of polyurethane foam, especially low density foam, in the presence of a hydrocarbon blowing agent which does not suffer from the above-mentioned deficiencies.

For this purpose, the use of compatibilizing agents has been investigated.

In a first aspect, this invention relates to a process for preparing a closed-celled polyurethane foam which includes reacting, in the presence of a hydrocarbon blowing agent, a polyisocyanate with a polyol composition wherein the polyol composition comprises:

- i) a polyether or polyester polyol having a hydroxyl number value of from 100 to 1200; and
- ii) from 5 to 25 parts, per 100 parts by total weight of the polyol composition, of a compatibilizing agent containing a compatibilizing radical of the formula



wherein n is a number greater than or equal to 5, and wherein the compatibilizing agent contains at least one active hydrogen atom, provided that there is no more than one aromatic group per molecule, and further wherein the compatibilizing agent is a fat, oil, monoglyceride, diglyceride, fatty acid, fatty alcohol, fatty amide, fatty amine, fatty acid ester, alkoxyated adduct of any of the foregoing, alkyl phenol or propoxylated adduct thereof, alkyl phenol or adduct thereof with ethylene oxide or propylene oxide, alkyl phenol or adduct thereof with less than an average of four molecules of ethylene oxide per molecule of alkyl phenol, or a mixture thereof.

In a second aspect, this invention is a process for preparing a closed-celled polyurethane foam which comprises reacting, in the presence of a hydrocarbon blowing agent, a polyisocyanate with a polyol composition, wherein the polyol composition comprises:

- i) a polyether or polyester polyol having a hydroxyl number value of from 100 to 1200; and includes:
- ii) from 5 to 25 parts, per 100 parts by total weight of the polyol composition, of a compatibilizing agent comprising a fat or oil having a hydroxyl number of from 100 to 550.

In a third aspect, this invention relates to a closed-celled polyurethane foam obtained according to an above-mentioned process.

In a fourth aspect, this invention relates to a blend, suitable for use in the inventive process as a polyurethane precursor composition, which comprises the above-mentioned polyol composition containing a compatibilizing agent as defined herein and further a blowing agent which is present in an amount of from 1 to 20 parts per 100 parts by

total weight of the composition and which is a C_{1-8} hydrocarbon, and preferably butane, n-pentane, i-pentane, hexane, cyclopentane, methylcyclopentane, cyclohexane, methylcyclohexane, isomer thereof, or a mixture of two or more thereof.

Surprisingly, it has been found that use of a compatibilizing agent as defined
5 enhances the miscibility of the hydrocarbon blowing agent and minimizes the susceptibility to separation of the formulation. The presence of the compatibilizing agent allows for an increased loading of the hydrocarbon blowing agent, thereby permitting the manufacture of foam having a lower density while retaining overall attractive physical properties.

The present invention relates to a process for preparing a rigid, closed-celled
10 polyurethane foam by reacting, in the presence of a hydrocarbon blowing agent, a polyisocyanate with a polyol composition comprising a certain compatibilizing agent. Advantageously, the resulting foam is of a low free rise density of from 10 to 50, preferably from 15 to 40, and more preferably from 15 to 35 kg/m³.

The polyurethane precursor composition comprises: (a) an isocyanate-reactive
15 component, usually a polyether or polyester polyol, having a hydroxyl number value of from 100 to 1200, preferably from 100 to 800, more preferably from 200 to 800, and yet more preferably from 200 to 600 and preferably being a polyester or polyether polyol; and (b) a compatibilizing agent. The compatibilizing agent allows for attractive miscibility of the hydrocarbon blowing agent with the polyol and is present in an amount of from 5 to 25,
20 preferably from 6, more preferably from 7, and preferably up to 18, more preferably up to 15 parts by total weight of the polyol composition including polyol and compatibilizing agent. The compatibilizing agent is defined herein as containing a compatibilizing radical of the formula



25 wherein n is a number greater than or equal to 5, and wherein the compatibilizing agent contains at least one active hydrogen atom, provided that there is no more than one aromatic group per molecule, wherein the compatibilizing agent is a fat, oil, monoglyceride, diglyceride, fatty acid, fatty alcohol, fatty amide, fatty amine, fatty acid ester, alkoxylated adduct of any of the foregoing, alkyl phenol, or propoxylated adduct thereof, alkyl phenol, or adduct thereof
30 with ethylene oxide or propylene oxide, alkyl phenol, or adduct thereof with less than an average of four molecules of ethylene oxide per molecule of alkyl phenol or a mixture thereof. In preferred embodiments each molecule contains only one active hydrogen atom.

The active hydrogen atoms contained in these compatibilizing agents are such as associated with hydroxyl, thiol, amine and carboxylic acid functionality. The presence of the
35 isocyanate reactive hydrogen atom is desired to permit reaction with the polyisocyanate, thereby incorporating, to the advantage of the polymer physical properties, the compatibilizing agent into the polyurethane polymer.

Advantageously, the compatibilizing agent is a fat, oil, or alkoxyated adduct thereof, with hydroxyl functionality and having a hydroxyl number value of from 100, preferably from 130, more preferably from 140, and up to 550, more preferably up to 300, still more preferably up to 200, and yet more preferably up to 180.

5 When fats or oils are selected, they preferably comprise a hydroxyl-substituted fatty acid constituent. Detailed descriptions of these materials and their fatty acid constituents are well known. See, for example, the entry "Fats and Fatty Oils" in Ullmann's *Encyclopedia of Industrial Chemistry*, ISBN 0-89573-160-6, or alternatively Kirk-Othmer *Encyclopedia of Chemical Technology*, ISBN 0-471-02062-1. For the present invention, suitable compatibilizing agents contain, as a fatty acid constituent, for example, ricinoleic acid, dihydroxystearic acid, 10 palmitic acid, stearic acid, oleic acid, linoleic acid, eicosanoic acid, or mixtures of two or more thereof. Preferred in one embodiment of the present invention is ricinoleic acid, which exhibits excellent miscibility with polar substances, such as alcohols including polyols, and limited miscibility with nonpolar substances such as hydrocarbons. A convenient and readily available natural fatty oil source comprising a hydroxyl-substituted fatty acid constituent is castor oil 15 which is understood to comprise on average 90 weight percent of a glyceride of ricinoleic acid, 4 weight percent of a glyceride of linoleic acid, with the balance to 100 percent of glycerides of dihydroxystearic acid, palmitic acid, stearic acid, oleic acid, linolenic acid and eicosanoic acid. Castor oil, essentially independent of source, has a hydroxyl number of from 160 to 168.

20 Suitable polyols include polyester or polyether polyols such as are conventionally used in the preparation of rigid polyurethane foam and having a hydroxyl number value within the above-mentioned range. Additionally, such polyols will generally contain from 2 to 8, preferably from 3 to 8, and more preferably from 3 to 6 hydroxyl groups per molecule. Examples of suitable, and preferred, polyols are polyether polyols as described more fully in 25 U.S. Patent 4,394,491. Exemplary of such polyether polyols include those commercially available under the trademark VORANOL, which include VORANOL 202, VORANOL 360, VORANOL 370, VORANOL 446, VORANOL 490, VORANOL 575, VORANOL 640, VORANOL 800, VORANOL CP1000, VORANOL CP260, VORANOL CP450, and VORANOL RN482, all available from The Dow Chemical Company. Other preferred polyols include alkylene oxide derivatives 30 of Mannich condensate as taught in, for example, U.S. Patents 3,297,597; 4,137,265 and 4,383,102; and amino-alkylpiperazine-initiated polyether polyols as described in U.S. Patents 4,704,410 and 4,704,411.

As mentioned, the polyurethane foaming process of this invention requires the presence of a hydrocarbon blowing agent which advantageously comprises a C_{1-8} aliphatic or 35 cycloaliphatic hydrocarbon, preferably C_{4-8} , which is an alkane, alkene or alkyne. Such hydrocarbons are selected as the blowing agent because they have a boiling point lower than the reaction exotherm, generally more than 120°C, and usually of from 150°C to 200°C, encountered when preparing a polyurethane foam. Suitable hydrocarbons include those

having a boiling point of less than 120°C, preferably less than 100°C, and more preferably less than 50°C such as, for example, butane, n-pentane, i-pentane, cyclopentane, methylcyclopentane, hexane, cyclohexane, methylcyclohexane, isomers thereof, or mixtures of two or more thereof. Preferred hydrocarbons, due to their ability to confer attractive thermal insulation properties to the polyurethane foam, are n-pentane, i-pentane and cyclopentane. Especially preferred is a mixture of isomers n-pentane and i-pentane wherein the ratio of n-pentane to i-pentane is from 5:95 to 50:50, preferably from 10:90 to 35:65. This fraction of i-pentane is found to be advantageous for optimum flow properties when preparing a polyurethane foam and for conferring attractive thermal insulation properties to the resulting foam. Typically the hydrocarbon will be present in an amount of from 1 to 20, preferably from 5 to 20, and more preferably from 7 to 18 parts per 100 parts by total weight of the composition comprising polyol and compatibilizing agent.

In addition to the hydrocarbon blowing agent, optionally a supplemental blowing means can be provided by the presence of water. Water reacts with polyisocyanate leading to the production of carbon dioxide which is able to confer a reduced density to the polyurethane polymer. When present, the amount of water advantageously is from 0.5 to 10, preferably from 1.5 to 8, and more preferably from 2 to 6 parts per 100 parts by weight of the polyol composition including the fatty oil. In a highly preferred embodiment of the invention, polyurethane foam is prepared in the presence of water and hydrocarbon blowing agent wherein, per 100 parts by weight of the polyol composition including the compatibilizing agent, the water is present in an amount of from 2 to 6 parts, and the hydrocarbon blowing agent being n-pentane, i-pentane, cyclopentane, or mixtures of at least two thereof is present in an amount of from 1 to 20 parts. In a lesser preferred embodiment, it is also possible to use conventional fluorocarbons or hydrogen-containing chlorofluorocarbons, as supplemental physical blowing agent, including difluorochloromethane, difluoroethane, difluorochloroethane, tetrafluoroethane dichlorotrifluoroethane and others such as those taught, for example, in U.S. Patent 4,945,119.

Suitable polyisocyanates include aromatic, aliphatic and cycloaliphatic polyisocyanates and combinations thereof. A crude polyisocyanate may also be used in the practice of this invention, such as the crude toluene diisocyanate obtained by the phosgenation of a mixture of toluene diamines or the crude diphenylmethane diisocyanate obtained by the phosgenation of crude methylene diphenylamine. Preferred are aromatic polyisocyanates comprising a methylene diphenylisocyanate, polymethylene polyphenylisocyanate, or mixtures thereof. Suitable mixtures include those containing, based on total weight of polyisocyanate, from 10 to 50 weight percent of methylene diphenylisocyanate; and from 90 to 50 weight percent of polymethylene polyphenylisocyanate. For the purpose of providing cross-linkages in the end polymer, advantageously such an aromatic polyisocyanate has an average isocyanate

functionality of at least 2.3, preferably from 2.5 to 3.5, and more preferably from 2.7 to 3.1. Exemplary of commercially available aromatic polyisocyanates suitable for use in this invention include crude methylene diphenylisocyanate mixtures supplied by The Dow Chemical Company under the trademark VORANATE and designated as M220, M229, M269, M595 and M580.

5 The amount of polyisocyanate present when preparing the polyurethane foam is such to provide for an isocyanate reaction index of typically from 60 to 550, preferably from 70, more preferably from 80, and preferably up to 300, more preferably up to 200, still more preferably up to 160, and yet more preferably up to 140. An isocyanate reaction index of 100 corresponds to one isocyanate group per isocyanate reactive hydrogen atom present including
10 those from the polyol composition containing compatibilizing agent and, if present, any water.

Optionally other ingredients may be present when preparing the polyurethane foam. Among these other ingredients are catalysts, surfactants, colorants, antioxidants, reinforcing agents, fillers, antistatic agents and flame retardants. Suitable flame retardants include phosphorus containing substances such as tris(chloroalkyl)phosphate and
15 trisalkylphosphates, for example triethylphosphate; and nitrogen-containing substances such as melamine.

One or more catalysts for the reaction of the active hydrogen-containing compound with the polyisocyanate are advantageously present. Suitable catalysts include tertiary amine compounds and organometallic compounds. Exemplary tertiary amine catalysts
20 include triethylenediamine, pentamethyldiethylenetriamine, N-ethylmorpholine, N-cocomorpholine, N-methylmorpholine, tetramethylethylenediamine, dimethylbenzylamine, 1-methyl-4-dimethylaminoethylpiperazine, 3-methoxy-N-dimethylpropylamine, diethylethanolamine, N,N-dimethyl-N',N'-dimethylisopropylpropylenediamine and N,N-diethyl-3-diethylaminopropylamine. Exemplary organometallic catalysts include organo-
25 mercury, organolead, organoferric and organotin catalysts, with organotin catalysts being preferred among these. Suitable tin catalysts include stannous chloride, tin salts of carboxylic acids such as dibutyltin di-2-ethyl hexanoate, as well as other organometallic compounds such as are disclosed in U.S. Patent 2,846,408. A catalyst for the trimerization of polyisocyanates and formation of polyisocyanurate polymers, such as an alkali metal alkoxide, alkali metal
30 carboxylate, or quaternary amine compound, may also optionally be employed herein. When employed, the quantity of catalyst used is sufficient to increase the rate of polymerization reaction. Precise quantities must be determined experimentally, but generally will range from 0.01 to 3.0 parts by weight per 100 parts polyol depending on the type and activity of the catalyst.

35 It is generally highly preferred to employ a minor amount of a surfactant to stabilize the foaming reaction mixture until it cures. Such surfactants, distinguished from the compatibilizing agent, are generally manufactured mineral oils including liquid or solid organosilicone surfactants. Other, less preferred surfactants, include amine salts of long chain

alkyl acid sulfate esters, and alkyl sulfonate esters and alkyl arylsulfonic acids. Such surfactants are employed in amounts sufficient to stabilize the foaming reaction mixture against collapse and the formation of large, uneven cells. Typically, from 0.1 to 3 parts of the surfactant per 100 parts by weight polyol are sufficient for this purpose.

5 In making a polyurethane foam, the polyol(s), polyisocyanate and other components are contacted, thoroughly mixed and permitted to expand and cure into a cellular polymer. The particular mixing apparatus is not critical, and various types of mixing head and spray apparatus are conveniently used. It is often convenient, but not necessary, to preblend some of the raw materials prior to reacting the polyisocyanate and active hydrogen-containing
10 components. For example, it is often useful to blend the polyol(s), blowing agent, surfactants, catalysts and other components except for polyisocyanates, and then contact this mixture with the polyisocyanate. Alternatively, all components can be introduced individually to the mixing zone where the polyisocyanate and polyol(s) are contacted. It is also possible to prereact all or a portion of the polyol(s) with the polyisocyanate to form a prepolymer, although such is not
15 preferred. For optimum processing, it is found convenient to prepare the polyurethane by mixing at an ambient temperature the reactants which themselves have a temperature of from 10°C to 35°C, and preferably from 15°C to 25°C.

The polyurethane foam obtained in accordance with this invention is of value for the appliance and construction industry where its attractive compressive strength, dimensional
20 stability and thermal insulation is highly desirable. The invention may also be used to provide polyurethane foam for semirigid applications such as for example sealant foam applications.

The invention is illustrated by way of the examples given hereinbelow. Unless otherwise indicated all amounts given are parts by weight.

Example 1

25 The storage stability of various hydrocarbon/-polyol mixtures optionally containing castor oil is reported in Table I. The substances and relative amounts making up the hydrocarbon and polyol mixtures are also given in Table I. The storage stability is determined in accordance with the following general procedure in which the hydrocarbon is blended into a polyol mixture, representative of a formulation typically used for the manufacture of rigid
30 polyurethane foam, and the resulting blend allowed to stand at room temperature for 7 days. After this period, the stability of the resulting blend is visually rated according to the following scheme:

- "Separates" - blend separates into multiple layers.
- "Turbid" - the turbid blend does not separate into multiple layers and
35 does not become clear on agitation.
- "Limit" - the turbid blend does not separate into multiple layers and on agitation becomes clear.

- "Separates" - blend separates into multiple layers.
- "Turbid" - the turbid blend does not separate into multiple layers and does not become clear on agitation.
- "Limit" - the turbid blend does not separate into multiple layers and on agitation becomes clear.
- "Clear" - the blend is clear and not separated into multiple layers.

Blends 1, 2 and 5 which separate are undesirable for the purposes of preparing a polyurethane foam; Blends 3 and 4 are observed to have a "clear" or "limit" status and are preferred as they are more readily manipulated in a consistent manner to the benefit of the foaming process.

Table I

parts by weight	Blend 1*	Blend 2*	Blend 3	Blend 4	Blend 5*
Castor Oil	0	3	7	10	28.5
Polyol 1	51	51	51	52.3	51
Polyol 2	14.3	14.3	14.3	12	14.3
Polyol 3	28.5	25.5	21.5	20	0
Surfactant 1	2	2	2	1.5	2
Catalyst	2.2	2.2	2.2	2.2	2.2
Water	2	2	2	2	2
i-pentane	10	10	10	10	10
n-pentane	3	3	3	3	3
Blend Stability after 7 days at:					
i) 20°C	/	Turbid	Limit	Clear	Separates
ii) 5°C	Separates	Separates	Turbid	Limit	Separates

* Not an example of this invention.

- Polyol 1: a sorbitol-initiated oxypropylene polyether polyol having a hydroxyl number of 480.
- Polyol 2: an ethylenediamine-initiated oxypropylene polyether polyol having a hydroxyl number of 640.
- Polyol 3: a glycerine-initiated oxypropylene polyether polyol having a hydroxyl number of 160.
- Surfactant 1: TEGOSTAB B8462 a silicon-based surfactant from Th Goldschmidt AG
- Catalyst: a blend of urethane promoting catalysts containing 1.2 pbw dimethylcyclohexylamine, 0.4 pbw pentamethyldiethylenetriamine; and 0.6 pbw of CURITHANE 206 a proprietary urethane promoting catalyst available from The Dow Chemical Company.

Example 2

Rigid polyurethane foam is machine-prepared in the presence of a hydrocarbon blowing agent and castor oil using the formulation as given in Table II. High pressure mixing conditions with reactants being introduced to the mixer head at a temperature of about 20°C are used. The results indicate that an improved blend stability is obtained while still maintaining an acceptable overall foam physical performance.

Table II

parts by weight	Foam 1*	Foam 2	Foam 3
Castor Oil	0	5	10
Polyol 1 ①	50	48	50.5
Polyol 2 ①	15	14	14
Polyol 3 ①	28.5	27	18.5
Surfactant 1 ①	2	1.5	1.5
Catalyst ①	2.2	2.2	2.2
Water	2.3	2.3	2.3
i-pentane	9.5	10	10
n-pentane	3	3	3
Isocyanate ② Index	115	115	115
Blend Stability after 7 days at 5°C	separates	limit	clear
Free Rise Density (kg/m ³)	22.6	21.7	22.4
Molded Foam properties, Density (kg/m ³)	34.3	32.6	32.9
Compressive Strength (kPa) (DIN 53421)	154.9	119.6	137
Thermal Conductivity (mW/M.k) (ASTM C-518)	23.1	23.5	23.2
Demold post expansion at 4 minutes (mm)	3.9	5	4.3

* Not an example of this invention.

① As given for Example 1.

② VORATEC SD100, a polymeric methylene diphenylisocyanate with an NCO functionality of 2.7, available from The Dow Chemical Company.

Example 3

The storage stability of various hydrocarbon/polyol mixtures containing compatibilizing agents other than castor oil is reported in Table III. The alternative compatibilizing agents and relative amounts making up the hydrocarbon and polyol mixtures is also given in Table III. The storage stability as reported is determined in accordance with the general procedure described for Example 1.

Table III

parts by weight	Blend 6*	Blend 7	Blend 8	Blend 9	Blend 10
Polyol 4	100	90	90	75	80
Cyclopentane	20	20	20	25	25
Compatibilizing Agent 1	0	10	0	0	0
Compatibilizing Agent 2	0	0	10	0	0
Compatibilizing Agent 3	0	0	0	25	0
Castor oil	0	0	0	0	20
Blend Stability at 20°C:	turbid	clear	clear	clear	clear

* Not an example of this invention.

15 Polyol 4: a sucrose/glycerine oxypropylene polyol having a hydroxyl number of 490.

Compatibilizing Agent 1: $C_{12}H_{25}-(OCH_2CH_2)_4-OH$

Compatibilizing Agent 2: $p(C_9H_{19})-C_6H_4-(OCH_2CH_2)_2-OH$

Compatibilizing Agent 3: monoglyceride adduct of oleic acid

20

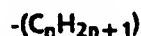
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1. A process for preparing a closed-celled polyurethane foam which comprises reacting, in the presence of a hydrocarbon blowing agent, a polyisocyanate with a polyol composition wherein the polyol composition comprises:

- i) a polyether or polyester polyol having a hydroxyl number value of from 100 to 1200; and
- ii) from 5 to 25 parts, per 100 parts by total weight of the polyol composition, of a compatibilizing agent containing a compatibilizing radical of the formula



wherein n is a number greater than or equal to 5, and wherein the compatibilizing agent contains at least one active hydrogen atom, provided that there is no more than one aromatic group per molecule, and further wherein the compatibilizing agent is a fat, oil, monoglyceride, diglyceride, fatty acid, fatty alcohol, fatty amide, fatty amine, fatty acid ester, alkoxylated adduct of any of the foregoing, alkyl phenol or propoxylated adduct thereof, alkyl phenol or adduct thereof with ethylene oxide or propylene oxide, alkyl phenol or adduct thereof with less than an average of four molecules of ethylene oxide per molecule of alkyl phenol; or mixtures thereof.

2. A process for preparing a closed-celled polyurethane foam which comprises reacting, in the presence of a hydrocarbon blowing agent, a polyisocyanate with a polyol composition wherein the polyol composition comprises:

- i) a polyether or polyester polyol having a hydroxyl number value of from 100 to 1200; and
- ii) from 5 to 25 parts, per 100 parts by total weight of the polyol composition, of a compatibilizing agent, a fat or oil or alkoxylated adduct thereof, having a hydroxyl number of from 100 to 550.

3. A process as claimed in Claims 1 or 2 wherein the hydrocarbon blowing agent comprises a C₁₋₈ aliphatic or cycloaliphatic hydrocarbon which is an alkane, alkene or alkyne.

4. A process as claimed in Claim 2 wherein the compatibilizing agent has a hydroxyl number of from 130 to 180.

5. A process as claimed in Claims 1 or 2 wherein the compatibilizing agent is a fat or oil comprising a fatty acid constituent.

6. A process as claimed in Claim 5 wherein the fatty acid constituent is ricinoleic acid, dihydroxystearic acid, palmitic acid, stearic acid, oleic acid, linoleic acid, eicosanoic acid, or a mixture of two or more thereof.

7. A process as claimed in Claim 6 wherein the fatty acid constituent is ricinoleic acid.

8. A process as claimed in Claims 1 or 2 wherein the compatibilizing agent is castor oil.

9. A process according to any one of Claims 1 to 8 which further comprises water in an amount of from 0.5 to 10 parts per 100 parts by total weight of the polyol composition.

10. A process for preparing a closed-celled polyurethane foam having a density of from 10 to 50 kg/m³ by reacting, in the presence of a hydrocarbon blowing agent, a polyisocyanate with a polyol composition wherein the polyol composition comprises:

i) a polyol composition containing a polyether polyol having a hydroxyl number value of from 100 to 1200, and including from 7 to 15 parts, per 100 parts by total weight of the polyol composition, of castor oil as a compatibilizing agent; in the presence of

ii) from 2 to 6 parts of water per 100 parts by weight of polyol composition; and

iii) a hydrocarbon blowing agent being n-pentane, i-pentane, hexane, cyclopentane, methyl-cyclopentane, cyclohexane, methylcyclohexane or mixtures thereof, and

wherein the polyisocyanate is present in an amount to provide for an isocyanate reaction index of from 60 to 550.

11. A blend, suitable as a polyurethane precursor, which contains a hydrocarbon and a polyol composition, wherein the composition comprises:

i) a polyether or polyester polyol having a hydroxyl number value of from 100 to 1200; and

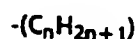
ii) from 5 to 25 parts, per 100 parts by total weight of the composition, of a compatibilizing agent which is a fat, oil or alkoxylated adduct thereof, having a hydroxyl number of from 100 to 550,

and wherein in the hydrocarbon, present in an amount of from 1 to 20 parts per 100 parts by total weight of said composition is butane, n-pentane, i-pentane, hexane, cyclopentane, methylcyclopentane, cyclohexane, methylcyclohexane, isomers thereof, or a mixture of two or more thereof.

12. A blend, suitable as a polyurethane precursor, which contains a hydrocarbon and a polyol composition, wherein the composition comprises:

i) a polyether or polyester polyol having a hydroxyl number value of from 100 to 1200; and

ii) from 5 to 25 parts, per 100 parts by total weight of the composition, of a compatibilizing agent containing a compatibilizing radical of the formula



wherein n is a number greater than or equal to 5, and wherein the compatibilizing agent contains at least one active hydrogen atom, provided that there is no more than one aromatic group per molecule, wherein the compatibilizing agent is a fat and oil, monoglyceride, diglyceride, fatty acid, fatty alcohol, fatty amide, fatty amine, fatty acid ester, alkoxylated adduct of any of the foregoing alkyl phenol or propoxylated adduct thereof, alkyl phenol or adduct thereof with ethylene oxide and propylene oxide, alkyl phenol or adduct thereof with less than an average of four molecules of ethylene oxide per molecule of alkyl phenol or a mixture thereof.

13. A polyurethane foam obtained according to a process as claimed in Claims

1 to 10.



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(71) Applicant: THE DOW CHEMICAL COMPANY (US/US); 2030 Dow Center, Abbott Road, Midland, MI 48640 (US).		Published With international search report.	
(72) Inventors: BIRCH, Adrian, J.; 23, avenue Adrien-Lachenal, CH-1290 Versoix (CH). FANICHET, Xavier, R., J.; Erlenstrasse 110, CH-8832 Wollerau (CH). LATHAM, Dwight, David; 313 Arrow Wood, Lake Jackson, TX 77566 (US). TABOR, Ricky, Lynn; 4600 Beechnut #206, Houston, TX 77096 (US).		(88) Date of publication of the international search report: 4 July 1996 (04.07.96)	
(74) Agent: DAMOCLES, Nemia, C.; The Dow Chemical Company, Patent Dept., P.O. Box 1967, Midland, MI 48641-1967 (US).			

(54) Title: A PROCESS FOR PREPARING POLYURETHANE FOAM IN THE PRESENCE OF A HYDROCARBON BLOWING AGENT

(57) Abstract

Disclosed is a process for preparing a rigid, hydrocarbon-blown, polyurethane foam by reacting a polyisocyanate with a polyurethane precursor composition comprising a polyol and a compatibilizing agent containing a compatibilizing radical of the formula: $-(C_6H_{2n-1})$ wherein n is a number greater than or equal to 5, and wherein the compatibilizing agent contains at least one active hydrogen atom, provided that there is no more than one aromatic group per molecule, and further wherein the compatibilizing agent is a fat, oil, monoglyceride, diglyceride, fatty acid, fatty alcohol, fatty amide, fatty amine, fatty acid ester, alkoxylated adduct of any of the foregoing, alkyl phenol or propoxylated adduct thereof, alkyl phenol or adduct thereof with ethylene oxide and propylene oxide, alkyl phenol or adduct thereof with less than an average of four molecules of ethylene oxide per molecule of alkyl phenol or a mixture thereof. A preferred compatibilizing agent is castor oil. The compatibilizing agent enhances the miscibility of the hydrocarbon blowing agent. Advantageously, the polyurethane precursor compositions exhibit improved storage stability.

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A CLASSIFICATION OF SUBJECT MATTER
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According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 6 C08J C08G

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	EP,A,0 445 614 (MOBAY CORP) 11 September 1991 see column 2, line 26-54 see column 4, line 56 see column 6, line 3-26 see claims ---	1,3,5-9, 12,13
A	EP,A,0 523 398 (BASF AG) 20 January 1993 see page 4, line 47-49 see page 7, line 54-57 see page 9, line 8-15 see page 15; example 9 see claims 1,6,7,9,16 ---	1,3,5-9, 12,13

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☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

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Date of the actual completion of the international search

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INTERNATIONAL SEARCH REPORT

International Application No.

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C (Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT		
Category	Citation of documents, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	EP.A.0 421 269 (BASF AG) 10 April 1991 see column 6, line 23-28 see column 7, line 50-53 see column 8, line 40-43 see column 11, line 18-42 see column 13, line 5-29 see claims 1-7,9 -----	1,3,5-9, 12,13

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/US 95/13313

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
EP-A-0445614	11-09-91	CA-A- 2037076	10-09-91
		JP-A- 4220457	11-08-92
		US-A- 5128087	07-07-92

EP-A-0523398	20-01-93	DE-A- 4121161	07-01-93
		CA-A- 2070209	28-12-92
		JP-A- 5209078	20-08-93
		US-A- 5205956	27-04-93
		US-A- 5300534	05-04-94
		US-A- 5278195	11-01-94

EP-A-0421269	10-04-91	DE-A- 3933335	11-04-91
		AT-T- 132882	15-01-96
		CA-A- 2024714	07-04-91
		DE-D- 59010045	22-02-96
		JP-A- 3152160	28-06-91
		US-A- 5096933	17-03-92
